

Development of the NIST Standard Sequential Extraction Protocol – Optimization for the Freshwater Lake Sediment SRM

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Numerous sites worldwide have been identified as having significant radioactive contamination, either as a result of routine or accidental releases. The radiological impact of this contamination depends on the extent to which the radionuclides are taken up by organisms, including humans. The mobility, and thus availability, of the radionuclides is greatly determined by the physico-chemical form (speciation) of the radionuclides in the soil or sediment in question.

One of the most common methods used to indirectly examine the speciation of radionuclides in the solid phase is the sequential extraction technique, which partitions a soil or sediment sample into operationally-defined sequentially-dissolved fractions (e.g., Nishita *et al.*, 1977; Cook *et al.*, 1984; Holm *et al.*, 1988; Bunzl *et al.*, 1995; Tronstad *et al.*, 1995; Schultz *et al.*, 1998). The association of the contaminant with the various fractions can then be used to examine its geochemical association and thus predict the environmental conditions under which it is likely to be released. For instance, a radionuclide adsorbed to the iron and manganese surface coatings of sediment grains will be subject to mobilization, as the nature of the surface changes, on transition from an oxic to an anoxic regime. The metal oxides will be solubilized and the radionuclides released to react with different mineral substrates.

A number of different sequential extraction protocols, with varying manipulative complexity, have been designed over the years. The choice of method will influence the

results, sometimes significantly. The chosen method should avoid, in so far as is possible, potential artifacts including, (1) readsorption (whereby an analyte is released during an extraction only to readsorb onto solid particles before the separation of the solid and liquid phases is possible) and (2) nonselectivity of extraction reagents (whereby the targeted geochemical phase is not uniquely attacked by the selected extraction medium). Many of the techniques used are based on modified sequential extraction protocols developed for use in soil chemistry and trace metal analysis (e.g., Gibbs, 1973; Jackson, 1973; Gupta and Chen, 1975; Tessier *et al.*, 1979).

We are developing a NIST Standard Sequential Extraction Protocol to allow comparison of the results of sequential extraction experiments undertaken by different laboratories. The protocol adopted (see Table 1) is based on a modified version of the method developed by Tessier *et al.* (1979) for fractionation of trace metals in marine particulate. In order to achieve this end, we are undertaking a study to evaluate the experimental conditions under which extraction selectivity is optimized for plutonium and uranium in two NIST Standard Reference Materials with different mineralogies (SRM 4357 Ocean Sediment and SRM 4354 Lake Sediment). The results of the first phase of the study (optimization of the protocol for the Ocean Sediment SRM) have already been published (Schultz *et al.*, 1997; Schultz *et al.*, 1998; Schultz *et al.*, 1998). The second phase of the study is now underway and preliminary results of the optimization of the Lake SRM will be presented and discussed.

Table 1. Summary of the sequential extraction method adopted

Fraction	Extractive Reagent	Reagent:Sample Ratio (mL/g)
Exchangeable	MgCl ₂ (pH 4.5)	15:1
Carbonates	NH ₄ Ac in 25% HAc (pH 4)	15:1
Oxides (Fe/Mn)	NH ₂ OH·HCl in 25% HAc, pH 2 (HNO ₃)	15:1
Organics	30% H ₂ O ₂ in 0.02 M HNO ₃ , pH 2	15:1
Acid Soluble	8M HNO ₃	15:1
Residual	Total dissolution	As required

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